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**Thermally Switchable Periodicities and Diffraction from Novel
Mesoscopically Ordered Materials**

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Abstract

Two novel switchable, mesoscopically periodic materials were created by combining crystalline colloidal array (CCA) self-assembly with the temperature-induced volume phase transition of poly(N-isopropylacrylamide) (PNIPAM). Body-centered cubic (BCC) CCA of hydrated, swollen PNIPAM particles Bragg diffract infrared (IR), visible, and ultraviolet (UV) light weakly, while arrays of compact shrunken particles diffract efficiently. A tunable diffracting array was also created by embedding a CCA of polystyrene spheres within a PNIPAM hydrogel, that swells and contracts with temperature; thus, the array lattice constant varies with temperature and the diffracted wavelength is thermally tunable across the entire visible spectrum. These materials may find applications in many areas of optics and materials science.

Monodisperse, concentrated, highly charged colloidal particles in very low ionic strength liquid media can self-assemble because of electrostatic repulsions to form crystalline colloidal arrays (CCA) (1-6). These ordered structures form BCC or face-centered cubic (FCC) arrays with lattice constants in the mesoscale size range (50 to 500 nm). Just as atomic crystals diffract x-rays that meet the Bragg condition, CCA diffract UV, visible, and near IR light (7); the diffraction phenomena resemble that of opals, which are close-packed arrays of monodisperse silica spheres (8). The CCA, however, can be prepared as macroscopically ordered arrays from non-close-packed spheres where Bragg diffraction is highly efficient. All light meeting the Bragg condition is diffracted while adjacent spectral regions freely transmit. Such arrays can be used as narrow-band optical diffraction filters (4,9-11) and have been proposed for use in novel nonlinear optical switching applications (12-14).

We recently proposed that CCA self-assembly could be used as a motif for creating solid, mesoscopically periodic materials (15). We developed methods to prepare a hydrogel network around the CCA, which permanently locks in the ordering (15,16). We now use this approach to create two novel periodic materials where either the size or the periodicity of the array can be switched.

We utilize the well-known temperature-induced volume phase transition of poly(N-isopropylacrylamide) (PNIPAM) (17-19) to create CCA materials with variable sphere size and array periodicity. In water below ~30 °C, PNIPAM is hydrated and swollen, but when heated above its lower critical solution temperature (~32 °C) it undergoes a reversible volume phase transition to a collapsed, dehydrated state. The

temperature increase causes the polymer to expel water and contract into a more hydrophobic polymer state.

We developed a synthesis of monodisperse, highly charged colloidal particles of PNIPAM using methods similar to that of Pelton and coworkers (20-21). Dispersion polymerization at $\sim 70^\circ\text{C}$ yielded collapsed colloidal spheres in the 100 nm size range. These colloidal particles exhibit a similar volume response to temperature as conventional macroscopic PNIPAM gels (22). For example, Fig. 1 shows the temperature dependence of the diameter of a typical preparation of PNIPAM colloids; the sphere diameter increases from ~ 100 nm at 40°C to ~ 300 nm at 10°C , which corresponds to a 27-fold increase in volume. Fig. 1 also shows the dependence of the turbidity of a dilute unordered dispersion of the same colloidal particles. The turbidity of this PNIPAM dispersion increases as the sphere diameter decreases at higher temperatures (23,24).

These PNIPAM colloids self-assemble in deionized water to form CCA both above and below the polymer phase transition temperature. The array diffracts light and closely follows (not exactly (7)) the Bragg diffraction law:

$$m\lambda = 2nd \sin \theta \quad (1)$$

where m is the integral order of diffraction, λ is the wavelength of incident light, n is the suspension refractive index, d is the interplanar spacing, and θ is the angle between the incident light and the diffracting crystal planes (7), which are oriented parallel to the crystal surface in the CCA we prepare. Fig. 2 shows the resulting extinction spectra of a PNIPAM CCA at 10° and 40°C . The lattice constant of the BCC array is 342 nm, and the nearest neighbor sphere distance is 242 nm. At low temperatures, the CCA particles are highly swollen, almost touching, and diffract weakly. Above the phase transition

temperature, the particles become compact and diffract nearly all incident light at the Bragg wavelength. The temperature change does not affect the lattice spacing; the 1-nm shift of the diffraction maximum wavelength upon heating from 10 ° to 40 °C results almost entirely from the change in the refractive index of water.

The CCA diffraction efficiency depends upon the colloidal particle scattering cross section as well as the array ordering. The particle size change alters the sphere scattering cross section, which in turn dramatically changes the diffraction efficiency (24). Therefore, this material acts as a thermally controlled optical switch as well as an optical limiter.

We can fabricate wavelength-tunable diffraction devices by using the volume phase transition properties of the PNIPAM gel to control the periodicity of a CCA. We dispersed monodisperse, highly-charged polystyrene (PS) spheres in an aqueous solution containing NIPAM monomer. The PS colloid self-assembled into a BCC CCA. We then photochemically initiated NIPAM polymerization to create a CCA embedded in a PNIPAM hydrogel film 125 to 500 μm thick (25). This polymerized CCA film (PCCA) shrinks and swells continuously and reversibly between 10 ° and 35 °C; the embedded PS sphere array follows, changing the lattice spacing and thus the diffracted wavelength.

The diffracted wavelength for the prepared PCCA film can be tuned between 704 and 460 nm by varying the temperature (Fig. 3). The inset to Fig. 3 shows the temperature dependence of the diffracted wavelength for this PCCA film where the incident light is normal to the (110) plane of the lattice. In addition to the change in the diffracted wavelength, the diffraction peak intensity increases as the volume decreases

because the diffraction intensity is proportional to the density of scatterers per layer, which increases as the material shrinks (7).

This PCCA film functions as an easily controlled tunable optical filter; the diffracted wavelength can be altered by varying either the temperature or the angle of incidence. At a fixed angle to the incident beam this PCCA acts as a tunable wavelength reflector. The width and height of the diffraction peak can be easily controlled by choosing colloidal particles of different size and refractive index or by making different thickness PCCA films (7). The tuning range of this device can be widened or narrowed by synthesizing PCCA films with higher or lower cross-linker concentrations.

We have created two novel mesoscopic periodic materials whose dimensions are controllable by temperature and can be used for light modulation in tunable diffracting and transmitting optical devices. These materials are likely to have additional technological applications for display devices and for image processing. For example, diffraction from these materials can be used to monitor the swelling properties of hydrogels. The diffracted wavelength gives detailed information on the gel volume, and an optical microscope could be used to examine the Bragg diffraction from small areas within the gel film to monitor gel phase transition homogeneity.

Figure Captions

Fig. 1. Temperature dependence of the PNIPAM colloid diameter and turbidity. The diameter was determined using a commercial quasielastic light scattering apparatus (Malvern Zetasizer 4). The turbidity was measured for a disordered dilute dispersion of these PNIPAM colloids by measuring light transmission through a 1.0 cm pathlength quartz cell with a UV-visible-near IR spectrophotometer. Solids content of the sample in the turbidity experiment was 0.071%, which corresponds to a particle concentration of 2.49×10^{12} spheres/cc.

Fig. 2. Diffraction from a CCA of PNIPAM spheres at 10 ° and at 40 °C. The spectra were recorded using a UV-visible-near IR spectrophotometer (Perkin Elmer λ -9). The dispersion was contained in a 1.0 mm quartz cuvette oriented at normal incidence to the incident beam. The observed diffraction switching behavior was reversible; these spectra were recorded after the seventh consecutive heat-cool cycle. Inset: Pictorial representation of the temperature switching between a swollen sphere array below the phase transition temperature and an identical compact sphere array above the transition.

Fig. 3. Temperature tuning of Bragg diffraction from a 125- μ m-thick PCCA film of 99-nm polystyrene spheres embedded in a PNIPAM gel. The diffraction wavelength shift results from the temperature-induced volume change of the gel, which alters the lattice spacing. Spectra were recorded in a UV-visible-near IR spectrophotometer with the sample placed normal to the incident light beam.

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21. The particles were formed by dispersion polymerization of 3.47 g N-isopropylacrylamide (main monomer), 0.03 g 2-acrylamido-2-methyl-1-propanesulfonic acid (ionic comonomer), 0.105 g N,N'-methylenebisacrylamide (cross-linker), 0.080 g sodium dodecyl sulfate (surfactant), and 0.014 g potassium persulfate (free-radical initiator) in 250 ml ultrapurified water at 70 °C for 4 hours. After synthesis the latex was purified by exhaustive ultracentrifugation and subsequent mixing with mixed-bed ion exchange resin. The ionic comonomer was added to provide additional surface charge to facilitate CCA formation.
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23. PNIPAM particles have unusual scattering properties because their size and refractive index are intimately related:

$$n_s = n_m \left(1 - \left(\frac{r_0}{r} \right)^3 \right) + n_p \left(\frac{r_0}{r} \right)^3 \quad (2)$$

where n_s , n_p , and n_m are respectively the sphere, polymer, and medium refractive indices, r is the sphere radius, r_0 is the radius of a completely collapsed, dehydrated sphere and the ratio $\left(\frac{r_0}{r} \right)^3$ represents the size-dependent volume fraction of polymer in the sphere. The Rayleigh-Gans approximation to Mie theory predicts the sphere scattering efficiency to be:

$$Q_{ext} = \frac{32}{27} \left(\frac{n_s}{n_m} - 1 \right)^2 \left(\frac{2\pi r}{\lambda} \right)^4 = \frac{32}{27} \left(\frac{16\pi^4 r_0^6}{\lambda^4 r^2} \right) \quad (3)$$

where n_s and r are the sphere refractive index and radius, n_m is the medium (water) refractive index, and λ is the wavelength of incident light (24). The refractive index factor dominates over the size factor in determining the scattering efficiency and the scattering decreases approximately as r^{-2} . We determined the scattering cross sections of the PNIPAM colloids by measuring the turbidity of a known concentration of particles. Our calculations of the scattering cross-sections based upon Rayleigh-Gans theory agree to within 20% of the measured scattering cross-sections.

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25. The PCCA was synthesized by photopolymerization of an ordered dispersion of 0.23 g monodisperse polystyrene colloids (99 nm, 19% solids), 0.35 g N-isopropylacrylamide (monomer), 0.02 g N,N'-methylenebisacrylamide (cross-linker),

and 0.004 g diethoxyacetophenone (UV photoinitiator) between two quartz plates separated by a parafilm spacer at ~ 2.0 °C. The polymerized film diffracted in a manner similar to the monomeric precursor. Careful purification (15) of all chemicals and sample cell components are required to achieve CCA self assembly; small concentration of ionic impurities will screen the electrostatic repulsive interactions.

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